(12) **EUROPEAN PATENT APPLICATION**

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(54) Conversion of propane to acrylic acid.

(57) Propane is converted to acrylic acid in an integrated three-stage process. Propane is dehydrogenated in a first stage to propylene, hydrogen, and by-products. The reaction effluent is passed into a second stage where propylene is oxidized to acrolein without significant oxidation of the hydrogen and by-products. The effluent from the second stage may be passed as feed to a third stage for the oxidation of acrolein to acrylic acid. The acrylic acid is recovered as the primary product, while the unconverted propane may be separated and recycled to the first stage for dehydrogenation.
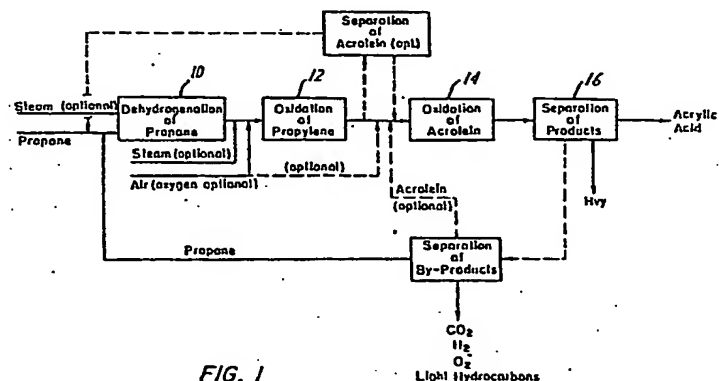
FIG. 1

EP 0 117 146 A1

Conversion of Propane to Acrylic Acid

The invention relates generally to the prepara-
tion of acrylic acid. More specifically the invention
5 relates to the preparation of acrylic acid in a three-
stage process from propane.

In typical processes of the prior art propylene
is reacted in the vapor phase with molecular oxygen over a
catalyst to produce acrolein. The reactor effluent
10 containing acrolein is then passed to a second oxidation
step where it is reacted with molecular oxygen in the
vapor phase over a different catalyst to form acrylic
acid. Generally, the feed for this process has been the
unsaturated olefin. Any saturated hydrocarbon present was
15 considered to be essentially an inert since little, if
any, oxidation occurred. Known dehydrogenation processes
could be used to prepare propylene from propane as a
feedstock for the known methods of preparing acrylic acid.
However, if propylene must be purified before oxidation,
20 then this would be an uneconomic way of preparing acrolein
and acrylic acid.

Integrated processes are not generally used
because the by-products of dehydrogenation cannot be
present in the subsequent use of propylene, without
25 causing contamination of the ultimate end product. The
present process relates to an integrated process in which
the dehydrogenation of propane is combined with the
oxidation of the resulting propylene to acrylic acid
without intermediate separation and purification of the
30 propylene before the oxidation is carried out.

In British Patent 1,340,891 propane and oxygen
are reacted to prepare propylene, acrolein, and acrylic
acid over a variety of base metal oxide catalysts. Since
the conversion of propane is quite low, high concentra-
35 tions of propane are used so that the net amount of
propylene produced is sufficient to result in a practical
process.

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U.S. Patent 4,260,822 also discloses a process for direct oxidation of propane to acrylic acid in a single step, again using large amounts of propane in order to overcome the relatively low conversion of propane to

5 the product.

The above one-step processes are not economic, since the conversions are quite low and require recycling of substantial amounts of unreacted feed in order to convert a high proportion of the propane fed. Also, the

10 catalysts typically do not have the long useful life necessary for satisfactory commercial operations.

A number of processes have been developed for converting propane to propylene. In U.S. Patent 3,784,483 a cobalt, iron, and phosphorus catalyst is disclosed as

15 useful for the oxidative dehydrogenation of propane to propylene.

In a group of patents exemplified by U.S. 4,083,883 a precious metal combined with promoter metals on a support is used for the dehydrogenation of paraffins,

20 particularly normal paraffins.

Another approach is taken in U.S. Patents 3,692,701, 4,005,985 and 4,041,099. In these processes large quantities of steam are used to dehydrogenate propane over a catalyst of platinum-tin on zinc aluminate.

25 Dehydrogenation of propane is shown over zinc titanate catalysts in U.S. 4,144,277 and 4,176,140.

Many patents have disclosed processes for oxidation of propylene to acrylic acid, such as EP 0000663 and U.S. 3,954,855. These processes are generally carried out

30 in two steps in order to obtain the best yields of acrylic acid. In the first step propylene is oxidized to acrolein in the vapor-phase over a promoted molybdenum catalyst and the effluent from the reaction is passed with added oxygen over a second promoted molybdenum catalyst to produce

35 acrylic acid.

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Based on the prior art discussed above, one might assemble a multi-step process wherein propane is dehydrogenated with or without the presence of oxygen to produce propylene, which would be separated and purified and fed

5   to a conventional acrylic acid process. In this way, substantially all of the propane fed is converted to acrylic acid by merely combining known processes. However, this may not be an economic way to produce acrylic acid. As will be seen, the present invention pertains to

10   an integrated process by which propane may be converted to acrylic acid without first purifying an intermediate propylene product.

Dehydrogenation of propane produces substantial amounts of hydrogen and small amounts of lower molecular

15   weight hydrocarbons, which in the prior art processes would be removed from the product, but which in an integrated process must be accommodated in the oxidation of propylene to acrolein. The hydrogen and by-products should not have an adverse effect on the oxidation

20   catalysts or their performance. For example, the exposure of the by-products to oxidizing conditions cannot produce contaminants which reduce the quality of the acrylic acid. Also, the presence of hydrogen should not create an explosive mixture in the oxidation reactors.

25   Summary of the Invention

Acrylic acid is prepared from propane in an integrated process in which dehydrogenation of propane to propylene in a first stage is followed immediately, that is, without separation and purification of the propylene

30   from the dehydrogenation effluent, by addition of oxygen and oxidation of the propylene to acrolein in a second stage. Alternatively, the dehydrogenation effluent may be cooled and water condensed and separated before the effluent stream enters the oxidation stage. The oxidation

35   stage may be followed by immediate oxidation of the

acrolein in the second stage effluent to acrylic acid in a third stage. Alternatively, the acrolein may be recovered or concentrated in the second stage effluent before being fed to the third stage for oxidation.

5   The acrylic acid product is recovered by scrubbing or quenching the third stage effluent which also contains unreacted propane, propylene, and oxygen, plus hydrogen, carbon oxides and miscellaneous light and heavy hydrocarbon by-products of the dehydrogenation and oxida-

10   tion reactions. Acrylic acid may be absorbed in water to separate it from the lighter by-products and unreacted feed components. Thereafter, at least unreacted propane is recycled. Residual gases depleted in acrylic acid may be scrubbed to recover propane and propylene, which are

15   recycled to the first stage for dehydrogenation. Alternatively, a selective oxidation may be employed to remove oxygen from the residual gases and carbon dioxide removed by scrubbing with a suitable solvent.

     The dehydrogenation of propane to propylene is

20   carried out by a vapor-phase reaction over a suitable catalyst, which may be platinum with or without a promoter on a zinc aluminate support or other suitable noble and base metal catalysts. When the catalyst is platinum, with or without a promoter, on zinc aluminate the dehydrogena-

25   tion will be carried out at about 400 to 700°C and up to about 10 kg/cm^2 gauge pressure, with a propane to steam ratio of about 1/0.5 to 1/10.

     The oxidation of propylene to acrolein and of acrolein to acrylic acid may be carried out over suitable

30   catalysts, such as mixed base metal oxides, especially molybdenum oxide-based catalysts.

Description of the Drawings

     Figure 1 is a block diagram showing the process of the invention.

35   Figure 2 is a simplified flowsheet showing one embodiment of the invention.

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Figure 3 is a simplified flowsheet showing an alternative embodiment of the invention.

<u>Description of the Preferred Embodiments</u>

In the principal aspect, the invention is an

5 integrated process combining the dehydrogenation of propane to propylene with the oxidation of the propylene to acrylic acid in two steps. The product acrylic acid is separated from the by-products and the unreacted propane may be recovered and recycled to the dehydrogenation step

10 if desired. A schematic view of such a complete process is shown in Figure 1.

The process contrasts with those of the prior art particularly in that the effluent from the dehydrogenation reaction 10 may be fed directly to the oxidation reaction

15 12 for conversion of propylene to acrolein. One familiar with the prior art would expect that propylene would be separated from the effluent of the dehydrogenation step 10 before feeding it to the oxidation step 12. Since the dehydrogenation of propane involves the production of sig-

20 nificant quantities of hydrogen, as well as small amounts of lower molecular weight hydrocarbons, the propylene must be oxidized in the presence of significant quantities of hydrogen, propane, and by-products, without markedly affecting the oxidation of propylene to acrolein or

25 causing oxidation of the hydrogen. We have found that propylene may be oxidized to methacrolein in the presence of hydrogen, propane, and by-products of the dehydrogenation step, while not adversely affecting the oxidation process.

30 After the propylene has been oxidized to acrolein, the entire effluent from the first oxidation step 12 may be sent directly to the second oxidation step 14 where the acrolein is oxidized to acrylic acid. Thereafter, the effluent of oxidation step 14 is partially condensed and

35 separated at 16. Purified acrylic acid is the product while the lower-boiling components are separated at 18.

Waste gases and heavy by-products are discharged while
unreacted propane is recycled to step 10. Alternatively,
oxygen and carbon oxides may be removed selectively and
the remaining gases recycled. Although acrolein will
5   normally be converted to acrylic acid and by-products, if
the conversion is kept at a lower level so that a
significant amount of acrolein remains, then acrolein
optionally may be recovered and recycled to the oxidation
stage 14 as shown.

10   In another aspect, the effluent from the first
oxidation step 12 may be separated to concentrate the
acrolein, which is then fed, along with air or oxygen to
the second oxidation step 14. Recovery may be made by
absorption in suitable liquids, such as water and the
15   lower carboxylic acids. Unreacted propane will be
returned to the dehydrogenation step 10 as shown.

Example 1

Dehydrogenation of Propane

        A catalyst composed of 0.4 wt % Pt and 1 wt % In
20   on a zinc aluminate support was prepared. A catalyst
sample of 50 cc as 3 mm extrudate was·charged to a tubular
reactor having a 25.4 mm i.d. An additional 250 cc of the
zinc aluminate support was added to the reactor above the
catalyst bed. A gas stream containing 1 mol of propane
25   for each 2 mols of steam was fed to the reactor at a gas
hourly space velocity of 4000 hr^{-1} under a pressure of
3.5 kg/cm^2 gauge. The inlet to the catalyst bed was
held at a predetermined temperature, with the outlet
temperature reflecting the endothermic nature of the
30   dehydrogenation reaction. The results are given below in
Table A.

Table A

Test	Inlet Temp.°C.	Conversion of Propane,%	Selectivity to Propylene,%
1	548	23.6	95.8
2	523	29.7	96.5

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The dehydrogenation of propane produces one mol
of hydrogen for each mol of propylene and additional
hydrogen from the formation of some lower molecular weight
by-products. When propylene is not separated before

5   subsequent oxidation the hydrogen and other by-products
are carried into the subsequent oxidation reaction.
Oxidation of the by-products to compounds which contam-
inate acrolein must be avoided. Oxidizing the hydrogen
along with propylene would be undesirable since it would

10 consume oxygen and interfere with the oxidation of pro-
pylene. Also, oxidation of hydrogen would generate
undesirable heat and could create hot-spots in the
catalyst and lower the production of acrolein. However,
it has been found that oxidation of propylene can be

15 carried out in the presence of hydrogen with substantially
no consumption of hydrogen, as will be seen in the follow-
ing example. The presence of propane which has not been
dehydrogenated also appears to have no significant effect
on the oxidation of propylene.

20   Example 2
                Oxidation of Propylene to Acrolein
          A catalyst was prepared according to the method
described in EP 0000663 and corresponding to Reference
Catalyst A and having composition of 80%

25 $K_{0.1}Ni_{2.5}Co_{4.5}Fe_3Bi_1P_{0.5}Mo_{12}O_x$ and 20% SiO_2. A charge
of 220 cc of catalyst as 4.7 mm pellets was placed in a
single-tube reactor having an i.d. of 12.7 mm. A feed
gas containing 5 vol% propylene, 20 vol % steam and 12%
oxygen was passed at a volume hourly space velocity of

30 1000-1200 hr^{-1} over the catalyst. The pressure in the
catalyst was about 1.76 kg/cm^2 gauge. Analysis by gas
chromatography of the effluent gases gave the results
designated in Tests 3-6 of Table A.

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Table A

Test No.	Time, hrs.	Temp. °C	Conversion of Propylene, %	Selectivity to Acrolein and Acrylic Acid, %
3	78.0	310	91.1	87.4
4	81.0	310	90.6	86.3
5	93.5	310	90.5	87.7
6	99.5	310	90.1	89.7
7	102	310	94.2	86.6
8	115	309	92.6	88.7
9	124	309	92.5	87.9
10	139	309	89.3	87.2
11	147	309	91.4	85.6
12	156	310	93.7	86.7
13	180	309	92.9	86.9

After the performance of the catalyst had been established with only propylene feed, hydrogen was added to the feed gas to simulate in part the conditions which would pertain to the oxidation reaction when supplied with propylene produced by dehydrogenation of propane. An additional 4 vol % of hydrogen was included with the mixture previously fed. The results are shown as Tests 7-10 in Table A. it will be seen that substantially the same results were achieved as in Tests 3-6. It was concluded that essentially no hydrogen was being oxidized, judging from the operating conditions in the reactor.

The hydrogen was discontinued and the oxidation reaction continued with 4 vol % propane added. The results are shown as tests 11-13 in Table A. Again substantially the same results were obtained as in Tests 3-6, indicating that propane was not affecting the oxidation of propylene and was not itself being oxidized.

These results show that propylene can be oxidized
in the presence of hydrogen and propane, the two principal
components of the dehydrogenation of propane to propylene.
It may be concluded that the integration of the
5 dehydrogenation and oxidation reactions is feasible.

Example 3

Oxidation of Acrolein to Acrylic Acid

To illustrate the oxidation of acrolein to
acrylic acid and the effect of hydrogen and propane
10 additions to the feed gas, experiments were carried out
which parallel those of Example 2.

A catalyst was prepared corresponding to the
composition of Example 1 of U.S. 3,954,855 and according
to the procedure described there. The catalyst composi-
15 tion was $Mo_{12}V_{4.8}Sr_{0.5}W_{2.4}Cu_{2.2}O_x$.
A 73 cc sample of the catalyst as 4.7 mm pellets was
placed in a tubular reactor having 12.7 mm i.d. The
reactor was surrounded by a bath thermostatically provid-
ing a uniform predetermined temperature. The feed to the
20 reactor was initially 6-8 vol % acrolein, 51 vol % air,
and 45 vol % steam. The volumetric space velocity was
3000 hr^{-1} and the average reactor pressure slightly
above atmospheric. The results are shown in Table B.

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Table B

</div>

Test No.	Time, hrs.	Temp. °C	Conversion of Acrolein, %	Selectivity to Acrylic Acid, %
14	126	254	92.8	89.1
15	126	251	84.5	89.2
16	41	252	86.8	88.4
17	36	251	80.7	87

As was done in Example 2, first 4 vol % hydrogen was added and then the hydrogen was replaced with propane. The results are shown in Table B as Test 16 (H_2) and 17 (propane). Although some difference in the conversion

5   of acrolein appears, it is clear from Tests 14 and 15 that conversion is very sensitive to temperature and the differences among Tests 15, 16, and 17 are not considered significant. The selectivity to acrylic acid is substantially the same. Again, it may be concluded that an

10   integrated process is feasible.

Separation of acrylic acid (16) may be done by methods known to the prior art. See for example, U.S. 3,926,744. The acrylic acid reactor effluent may be quenched with water or a high-boiling point solvent.

15   Acrylic acid can be removed from the aqueous solution by solvent extraction with a suitable liquid, e.g. ethyl acetate. The resulting acrylic acid-solvent solutions may be separated and purified by distillation to produce acrylic acid.

20   In its broadest form, the invention includes the integration of dehydrogenation and two oxidation stages whereby the propane is converted to acrylic acid, after which unreacted propane is recycled. Such a combination process without an intermediate separation of propylene

25   has been shown to be possible. If the resulting by-product stream containing significant quantities of propylene and propane can be used for other purposes, then recycling of the gas is not required. In many cases, it will be desirable to recycle unreacted propylene and propane so

30   that the integrated process substantially converts propane to acrylic acid with only minor amounts of by-products and without ever producing a substantially pure propylene stream. In order to recycle gas containing large amounts of propane, it will be necessary to remove hydrogen

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produced in the dehydrogenation step, excess oxygen from
the oxidation step, and carbon oxides formed in all three
steps. In addition, a purge of light and heavy by-pro-
ducts and feed impurities will be taken. Removal of

5 carbon dioxide typically would be done by scrubbing all or
a portion of the recycle stream with a carbonate or amine
solution as is known in the art in order to maintain the
desired level of carbon dioxide. Carbon monoxide will be
converted to carbon dioxide in the dehydrogenation

10 reactor. Since the presence of these materials is not
critical to either the dehydrogenation or oxidation steps,
they may be economically permitted to build up in the
recycle stream to a level in which they may be
conveniently and economically removed. Since the light

15 and heavy hydrocarbon by-products, such as methane,
ethane, ethylene, butane, and butenes boil at temperatures
significantly different from those of acrolein or the
C_3 hydrocarbons, they may be separated by distillation.
Alternatively, streams containing the by-products in

20 concentrated amounts may be purged. Separation of the
hydrogen formed by the dehydrogenation of propane might be
done by various methods such as catalytic oxidation,
liquid phase absorption or gas phase adsorption.

Figure 2 is a simplified flowsheet showing a pre-

25 ferred embodiment of the invention with a complete process
whereby propane is converted substantially to acrylic
acid. Fresh propane feed 20 is combined with recycle
stream 24 containing principally propane and vaporized in
exchanger 22. The combined stream 26 is then heated in

30 exchanger 28 to a temperature such that when combined with
the required amount of steam (30) the temperature obtained
will be that suited for the dehydrogenation of propane to
propylene. The amount of steam used preferably is
suitable for the subsequent oxidation of the propylene to

35 acrolein.

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As shown here, steam is supplied as a fresh feed stream.
If this is done, then water produced in the reactions is
eventually purged from the system from the bottom of the
stripper 56. A feed stream containing propane and steam
5   in molar ratios between 1/0.5 and 1/10, preferably 1/1 to
1/5, is fed at temperatures between about 400-700°C,
particularly about 600°C, and at pressures up to about
0-10 kg/cm^2 gauge, preferably near 0 kg/cm^2 gauge,
to reactor 32 where about 50% of the propane is converted
10   to propylene, with a selectivity of 75% or more.

        A number of catalysts have been disclosed in the
prior art for use in this process and the conditions under
which the reaction is carried out will depend on the
catalyst selected. Of particular usefulness is a
15   platinum-based catalyst of the type shown in U.S.
4,005,985. Although platinum and tin disposed on a zinc
aluminate support provides good performance, other
catalysts which have been found effective include platinum
and other promoters, such as rhenium and indium supported
20   on zinc aluminate. Other Group VIII noble metals, alone
or in combination on various supports known to the art may
have application in the dehydrogenation of propane to
propylene.

        Other potential supports would include alumina,
25   other alkaline earth metal aluminates, and rare earth
aluminates including lanthanum. Promoters such as tin,
lead, antimony, and thallium may be used. Base metal
catalysts such as the chromium, zirconium, titanium,
magnesium and vanadium oxides as shown in U.S. 3,479,416
30   and 3,784,483 or the zinc titanate of U.S. 4,176,140 and
4,144,277 also might be used. The invention is not con-
sidered to be limited to specific catalyst formulations.

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It will be understood by those skilled in the art
that in this process the catalyst rapidly deactivates and
must be regenerated frequently. Typically, the process
will be operated with multiple reactors so that frequent
5   regeneration is possible. The details of such operations
are, however, not considered part of the invention. The
dehydrogenation reaction is endothermic and the tempera-
ture leaving the reactor 32 will be on the order of
50-200°C lower than the inlet temperature. This will be
10 affected by the amount of steam employed, the condition of
the catalyst, and the severity of the reaction conditions
chosen.

The dehydrogenation reactor effluent is cooled in
exchanger 34 to a suitable temperature for inlet to the
15 oxidation reactor 38 and joined with an oxygen-containing
stream 36 to provide a suitable feed for the oxidation of
propylene to acrolein. Air enriched in oxygen or air
alone might be used, if economic to do so. Although not
shown in this flowsheet, it is also possible to cool the
20 effluent from reactor 32 until water is condensed from the
gases. Removal of the water would permit adjustment of
the steam to propylene ratio used in oxidation reactor 38.
The reaction would be carried out under conditions typical
of the art, that is, temperatures in the range of about
25 200-600°C, usually about 300-350°C, pressures of about 0-5
kg/cm^2 gauge, and gas hourly space velocities on the
order of 2000 hrs^{-1}. A suitable oxidation catalyst
will be used, typically a mixture of base metal oxides,
especially those which are molybdenum-based. The reactor
30 typically will be of the tubular type where the pelleted
catalyst is placed inside tubes which are surrounded by a
heat transfer fluid for the removal of the heat of reac-
tion. Typically, 90-95% of the propylene feed to the
reactor will be converted to acrolein, along with minor
35 amounts of acrylic acid, acetic acid, and less significant

quantities of lighter and heavier by-products. Some of
the propylene is burned to carbon oxides and water.

The effluent from reactor 38 is fed with or
without intermediate heat exchange and adjustment of the
5   gas composition to reactor 40, where the acrolein is
converted to acrylic acid. The reaction would be carried
out under conditions typical of the art, that is, tempera-
tures in the range of about 200-600°C, usually about 250-
300°C, pressures of about 0-5 kg/cm^2 gauge, and gas
10   hourly space velocities on the order of 2000 hrs^{-1}. A
suitable oxidation catalyst will be used, typically a
mixture of base metal oxides, especially those which are
molybdenum-based. The reactor configuration will be
similar to that of reactor 38. Typically 90-98% of the
15   acrolein fed to the reactor 40 will be converted to
acrylic acid, and minor amounts of acetic acid, carbon
oxides, and other by-products. Overall, the selectivity
of propylene to acrylic acid would be about 75-80%.

The resulting gaseous mixture may be cooled and
20 fed to an quench tower 42 where an acrylic acid-water
mixture is condensed in a recirculating aqueous stream 44
at temperatures in the range of about 30-50°C. Substan-
tially all of the acrylic acid is recovered in a solution
containing up to about 35 mol % acrylic acid. This
25   solution is sent to an extraction column 46 where the
acrylic acid is selectively extracted by a recirculating
stream of a suitable solvent, such as ethyl acetate. The
solvent rich with acrylic acid is passed to a stripper 48
to recover the solvent for recycle via line 50. Acrylic
30   acid is passed via line 51 to two additional columns 52
and 54 for separation of the lighter and heavier
impurities. Water produced in the process is removed from
the bottom of column 46 via stream 47 and sent to stripper
56 for removal of hydrocarbons and then disposed of or
35   recirculated as steam to the dehydrogenation step.

The light gases leaving the top of the quench tower 42 contain large quantities of propane along with lesser amounts of propylene, carbon oxides, hydrogen, oxygen, nitrogen, and light impurities. These gases are

5 passed to absorber 58 for recovery of the C_3 content if they are to be returned for further conversion to acrylic acid. Suitable solvents which may be employed include paraffin or aromatic hydrocarbons. Light gases are vented from the process from the top of tower 58. The

10 solvent rich in C_3's is passed to column 60 where they are stripped out and returned to reactor 20 via line 24.

In an alternative embodiment, the gases from absorber 42 could be passed to a reactor where the oxygen content is consumed by reaction with the hydrogen present.

15 This selective oxidation may be carried out over suitable catalysts, such as platinum on alumina, which can carry out the oxidation at a sufficiently low temperature that the valuable C_3 hydrocarbons are not oxidized and lost. Once the oxygen has been consumed the gas may be

20 returned to the dehydrogenation reactor, preferably after a slip stream having been scrubbed to remove the carbon dioxide produced by the oxidation steps and to separate C_3's from light by-products, which are purged.

An example of the practical operation of the

25 flow sheet shown in Figure 2 is as follows:

Example 4

One hundred mols/hr of a feed stream 20 containing 99% propane is vaporized in exchanger 22 and fed to the dehydrogenation reactor 32, along with 240

30 mols/hr of a recycle propane stream 24. The combined streams 26 are heated to about 675°C (28) and mixed with 560 mol/hr of steam (30) which may be provided by

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recycling and vaporizing stream 49 from the stripper 56. The combined stream 29 is fed to the dehydrogenation reactor 32, where about 29% of the propane fed is converted with 80% selectivity to propylene over a

5 promoted platinum catalyst. Leaving the reactor 32 at about 600°C, the effluent stream is cooled to about 125°C in exchanger 34 and mixed with 152 mol/hr of oxygen (36) before being supplied to the oxidation reactor 38, where about 93% of the propylene is converted with 88%

10 selectivity to acrolein over a promoted molybdenum catalyst. Leaving the reactor 38 at about 325°C and 1.4 kg/cm^2 gauge the effluent gases are passed to the second oxidation reactor 40 for conversion of acrolein to acrylic acid. Leaving the reactor (40) at about 270°C and

15 1.0 kg/cm^2 gauge the effluent steam is cooled to about 140°C and enters quench tower 42 where water, acrolein, and acrylic acid are condensed and absorbed in a recirculating stream 44, cooled to about 35°C in exchanger 43.

The crude recycle gas leaving the top of the

20 absorber 42 is passed to absorber 58 where it is contacted with a recirculating stream of 250 mol/hr containing C$_8$ paraffins to recover substantially all of the C$_3$ content. The waste gases, i.e. 250 mol/hr of hydrogen, oxygen, nitrogen, and light by-products, are

25 vented from the top of column 58. The enriched liqu'd is stripped in column 60 and 240 mol/hr of propane is recovered and recycled via line 24 to dehydrogenation reactor 32.

An aqueous stream of 550 mol/hr containing 12

30 mol % acrylic acid, along with acrolein and miscellaneous by-products such as acetic acid, maleic acid, formic acid, and other oxygenated compounds is passed to extractor 46

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where it passes countercurrently versus 190 mol/hr lean
solvent (ethyl acetate) entering the base of the tower via
line 50. Substantially all of the acrylic acid is
absorbed. Water raffinate is withdrawn from the bottom of
5   column 46 and passed via line 47 to column 56 where light
by-products are distilled overhead and withdrawn as a
waste stream. Stripped water is withdrawn (49) from the
bottom of the column for reuse or disposal. The enriched
solvent passes overhead from column 46 and is distilled in
10   column 48 to separate the solvent which is recovered
overhead and recirculated to column 46 via line 50. The
crude acrylic acid leaves the bottom of column 48 and is
sent to column 52 via line 51.

          The crude acrylic acid stream of 70 mol/hr
15   comprises 90 mol % acrylic acid, with the remainder acetic
acid, ethyl acetate and heavy by-products. Light
impurities and any residual water are distilled overhead
and passed via line 53 to column 56. Partially purified
acrylic acid is sent to column 54 via line 55 where it is
20   distilled away from the heavy by-products and withdrawn
as a sidestream. High boiling waste materials such as
maleic acid are withdrawn from the bottom of column 54 for
disposal. Any residual light materials are sent to column
56.

25   Figure 3 is a simplified flow sheet showing an
alternative embodiment of the invention where acrolein is
recovered and purified from the effluent of reactor 38
before being oxidized to acrylic acid in reactor 40. The
previous discussion of the dehydrogenation and first
30   oxidation steps is still pertinent. In this embodiment,
the effluent from reactor 38 is cooled and then led to a
quench tower 39A where acrolein is scrubbed from the gases
by a recirculating aqueous stream. Gases which are not

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absorbed may be purged or preferably, the C_3 content
of the gases is separated by absorption or the like and
returned to reactor 32 via line 24. After being absorbed
in tower 39A, the enriched absorbent is stripped in tower

5   39B to provide stream rich in acrolein to the second
oxidation reactor 40 via line 39C. Air or oxygen is added
and the oxidation to acrylic acid is carried out as
previously described. Recovery of the acrylic acid from
the reactor effluent proceeds as in Figure 2, as does the

10 purification of acrylic acid.

          An example of the operation of the process shown
in Figure 3 is as follows:

Example 5

          One hundred mols/hr of a feed stream 20 contain-

15 ing 99% propane is dehydrogenated to propylene and then
oxidized to acrolein under the conditions of Example 4
except that upon leaving reactor 38 the effluent is cooled
to 120°C and fed to absorber 39A, where the acrolein is
scrubbed out by countercurrent contact with water. The

20 rich absorbent is stripped in column 39B by vapor supplied
by the reboiler. The light gases are returned to the
dehydrogenation reactor 32 while 64 mol/hr of acrolein,
along with minor amounts of by-products are sent via line
39C to the second oxidation reactor 40. The remainder of

25 the flow sheet is substantially the same as that shown in
Figure 2.

          Although in its principal aspects the invention
is directed to the preparation of acrylic acid from
propane, it should be understood that acrolein can be

30 recovered from the effluent of the first oxidation
reactor, as shown in Figure 3 for example, and used as a
product of the process where acrolein is needed for
various end uses, such as preparation of allyl alcohol.

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CLAIMS

1. A process for the preparation of acrylic acid from propane comprising:

(a) in a first stage dehydrogenating propane to propylene, optionally in the presence of steam, over a dehydrogenation catalyst to form an effluent stream comprising propylene, hydrogen, carbon oxides and unreacted propane;

(b) in a second stage mixing oxygen and optionally steam with said effluent stream of (a) and passing the mixture over a first oxidation catalyst at conditions selected to produce a second effluent stream comprising acrolein, unreacted propylene and propane, and oxygen, hydrogen and carbon oxides;

(c) in a third stage passing the effluent stream of (b) optionally with additional oxygen over a second oxidation catalyst at conditions selected to produce a third effluent stream comprising acrylic acid, unreacted propylene, propane and acrolein, and oxygen, hydrogen, and carbon oxides;

(d) recovering the acrylic acid from said effluent of (c) to produce an acrylic acid-depleted effluent; and

(e) returning at least the unreacted propane from said acrylic acid-depleted effluent to step (a).

2. The process of claim 1 wherein said dehydrogenation stage (a) is fed with propane and steam in a ratio of about 1/0.5 to 1/10 and a temperature about 400-700°C and a pressure up to about 10 kg/cm^2 gauge.

3. The process of claim 1 or claim 2 wherein said dehydrogenation stage (a) employs a catalyst comprising a Group VIII noble metal or a base metal oxide on a support.

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4.   A process as claimed in any one of claims
1 to 3 characterized in that the effluent stream of (a)
is cooled and water is condensed and separated there-
from before said effluent stream enters the second stage
of (b).

5.   A process as claimed in any one of claims 1
to 4 characterized in that said effluent of (c) is
cooled to condense water therefrom and acrylic acid is
recovered as an aqueous solution, thereby forming a
residual effluent gaseous stream comprising unreacted
propylene, propane, and acrolein, and oxygen and
carbon oxides.

6.   A process as claimed in claim 5 characterized
in that the propylene, propane, and acrolein of said
residual gaseous stream are absorbed in a suitable
solvent and thereafter recovered from said solvent and
returned to step (a).

7.   A process as claimed in claim 5 characterized
in that said residual gaseous stream is passed over a
suitable catalyst at selective oxidation conditions for
removal of said oxygen by reaction with hydrogen and
thereafter returned to step (a).

8.   A process as claimed in any one of claims 1
to 7 characterized in that the effluent stream of step
(b) is contact with a solvent to increase the acrolein
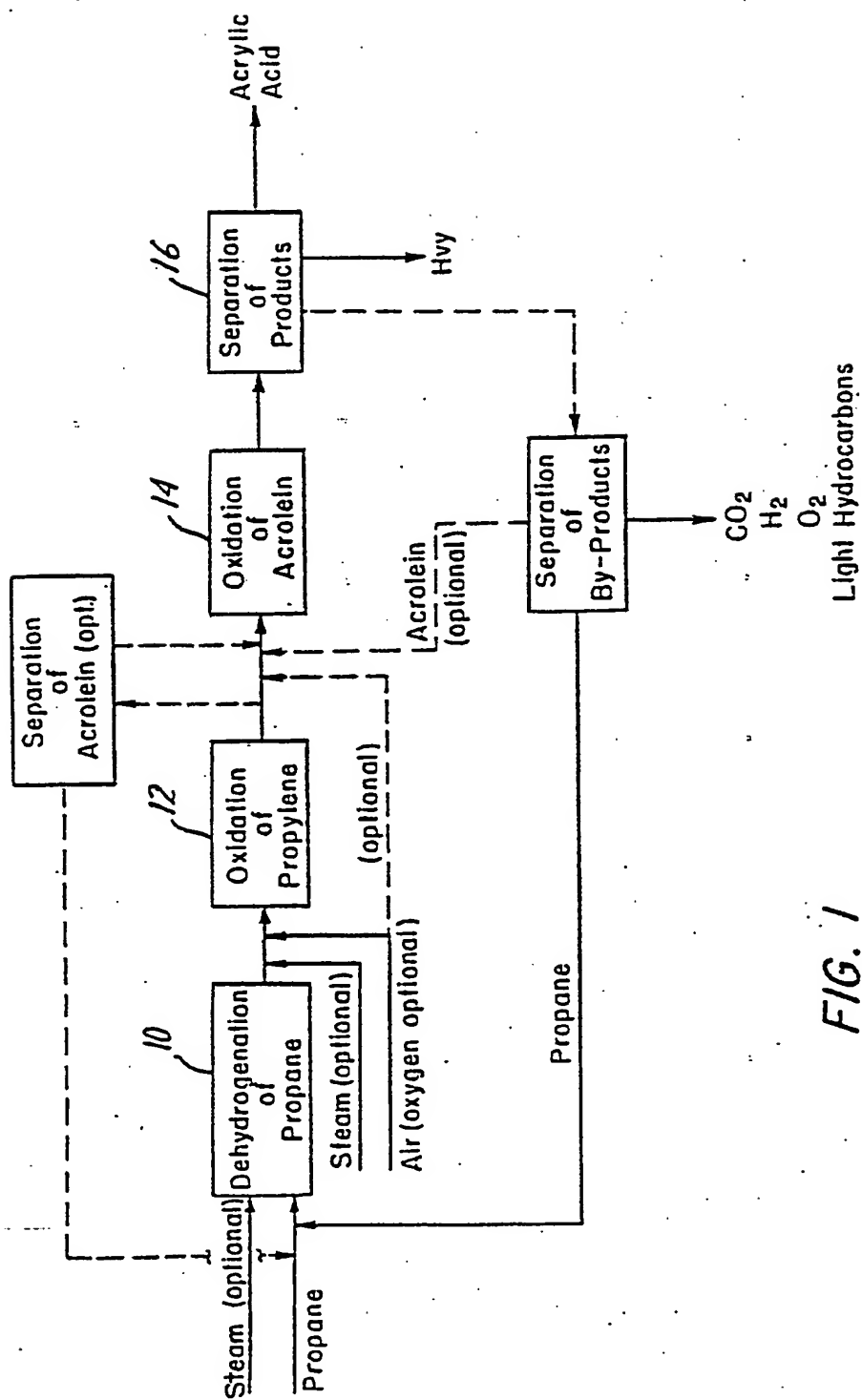content of said effluent stream passing over said second
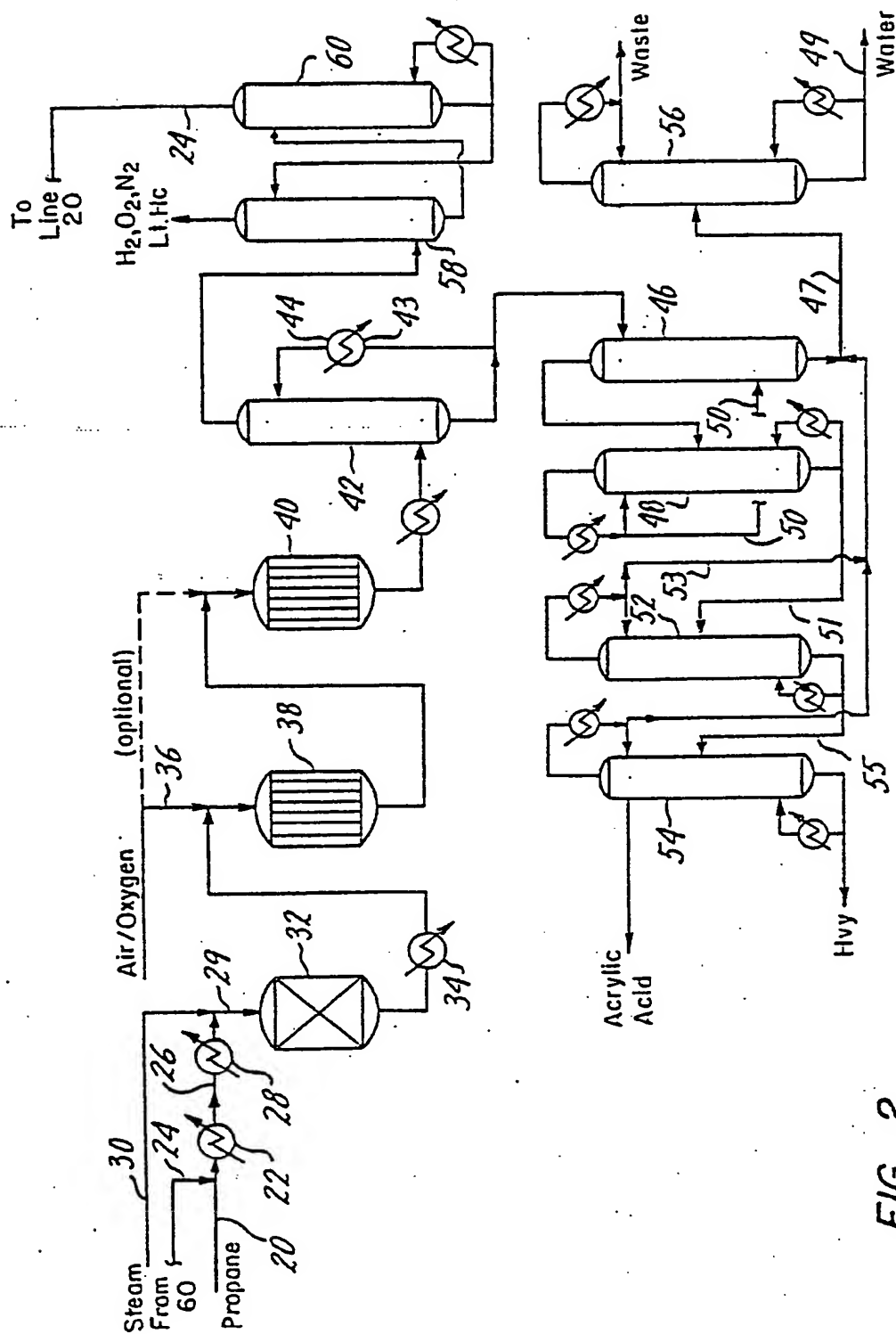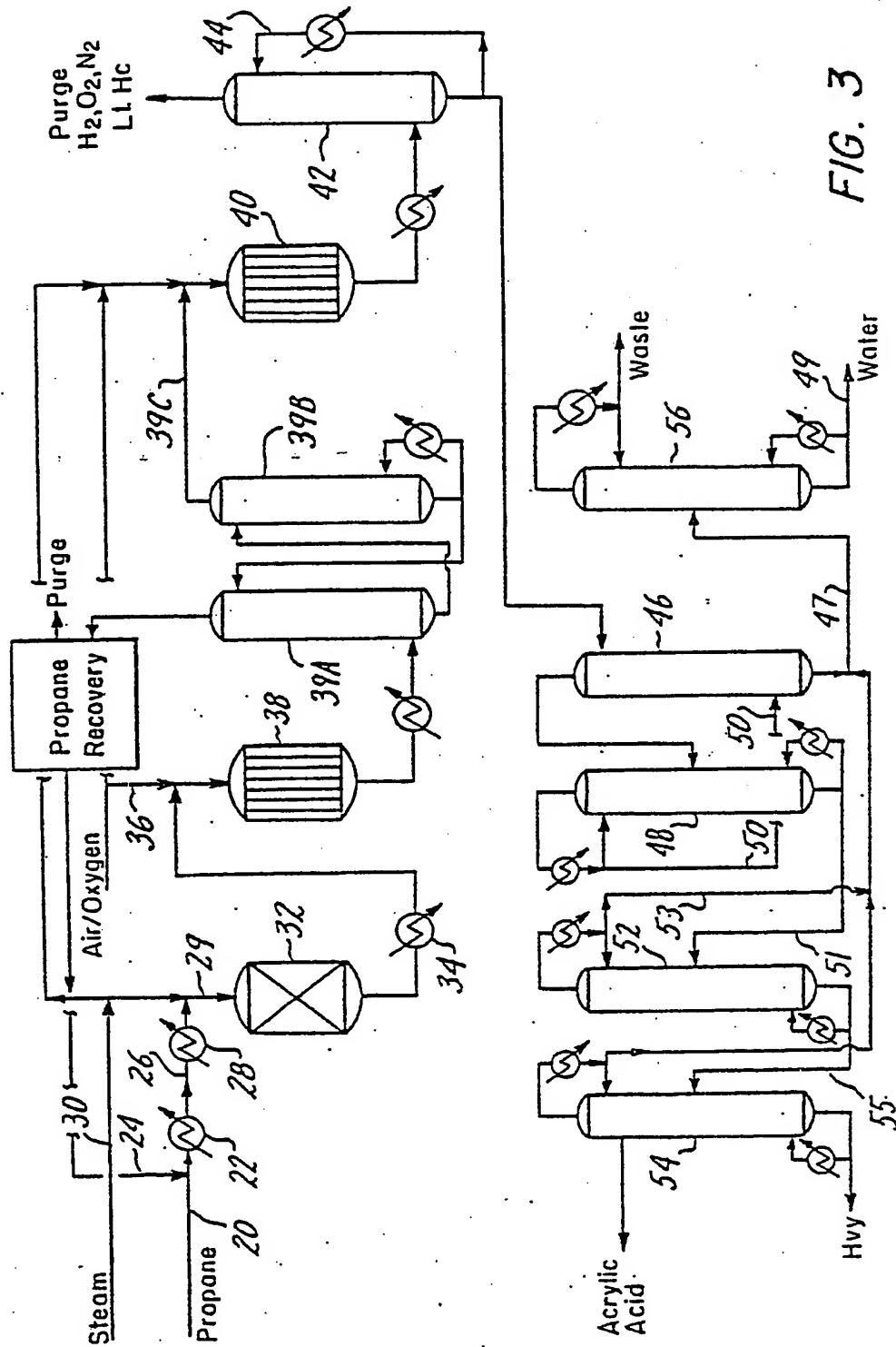oxidation catalyst.

FIG. 1

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FIG. 2

Purge
H2,O2,N2
Ll Hc

44

42

40

39C

39B

Purge

38

39A

Propane
Recovery

36

Air/Oxygen

29

32

34

30

24

26

22

28

20

Steam

Propane

Waste

56

49

Water

46

47

50

48

50

52

53

51

54

55

Hvy

Acrylic
Acid

FIG. 3

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
E	GB-A-2 118 939 (THE HALCON SD) * Whole document * -----	1-4,6-8	C 07 C 51/215 C 07 C 51/25 C 07 C 57/04 C 07 C 5/333 C 07 C 11/06 C 07 C 45/35 C 07 C 47/22

TECHNICAL FIELDS
SEARCHED (Int. Cl. ³)

C 07 C 51/00
C 07 C 57/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25-05-1984	KLAG M.J.